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CATALYST PREPARATION FROM VARIOUS NATURALLY AVAILABLE WASTE MATERIALS FOR BIODIESEL PRODUCTION: A REVIEW

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ABSTRACT

The fossil fuels, which are non-renewable are depleted at a faster rate and leading to the issue of energy crises. Therefore, it is necessary to look for a fuel source that will substitute the fossil fuel and meets the energy requirement. Biodiesel is considered as a promising fuel and can be produced from vegetable oils, naturally available plants and organic waste and also from non-edible oils. The process of biodiesel production from transesterification reduces the issue of dependency on non-renewable resources. The drawbacks associated with the process are higher production cost, final product has to be purified and the process has technical limitations such as operating conditions and the catalyst used. Therefore, the transesterification process has to be modified with respect to the operating conditions and the expensive catalyst. The catalyst required can be produced from naturally available waste materials which reduce the cost of the overall process. The calcium oxide produced from the waste materials can be used as the catalyst for the production of biodiesel. The present study reviews the production of calcium oxide as catalyst from various naturally available waste materials for transesterification process.

KEYWORDS: Biodiesel, Catalyst, Natural Waste, Characterization & Calcium Oxide

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Original Article

1. INTRODUCTION

The fast growth of industries and improvement in technology has necessitated the rapid usage of oil in the society [1]. The world is depending on the fossil fuels to satisfy the excess demand for energy requirement. Therefore, the non-renewable sources such as oil, coal and gas are getting depleted rapidly day by day [2, 4]. The consumption of these resources pollutes the environment by increasing the carbon dioxide concentration in the atmosphere [5]. This leads to the issue of global warming, which in turn affects the environment [6]. Thus, the sharp depleting of fossil fuels led to a search for an alternative source of fuel, which is preferably renewable source [7]. Energy can be produced from various renewable sources like tidal, nuclear, geothermal, solar and biomass [8]. Also, there is a requirement to produce alternative energy source, which is cheap and efficient. Thus, it is required to find alternative source of fuel which is environment friendly [9]. The biodiesel produced from biomass is considered to be effective and potential alternative source to fossil fuel.

Various methods are used for the production of biodiesel such as pyrolysis, microwave technique, supercritical method, ultrasonic method, reactive distillation, membrane process and transesterification using the catalyst [10, 11]. Transesterification of the oil with the help of catalyst is a promising method for the production of biodiesel [13]. Biodiesel produced has the advantages that it is non-toxic, environment friendly, biodegradable and sustainable in nature [14]. The properties of the biofuel are same as that of diesel fuel, where it is used for

transportation purpose. It has less sulphur content, improved cetane number emits less quantity of greenhouse gases compared to diesel [15, 16]. It was encouraged by the ministry of renewable energy that the biodiesel is used for transportation sector, and biofuel may be blended with petroleum so that the market demand can be solved [17]. The biodiesel production will provide job opportunities in undeveloped regions, environmental protection is prevented and economy can be improved [18]. Different feed stocks like edible oil, non-edible oil, used cooking oil, animal fat can be used for the feed oil for biodiesel production [19]. Edible oils like corn, sunflower, peanut and soybean oil are one of the feed for biodiesel production. But, because of issue of food security faced and the rise in price of oil in the global market, the use of edible oil for biodiesel is restricted [20, 21]. Thus, the researchers are thinking for the production of biodiesel from various naturally available feedstocks. The conventional catalysts used are expensive and technical constraints exists. Therefore, the current paper investigates the various naturally available materials used for preparing calcium oxide as catalyst for transesterification process. It also studies various techniques used for the characterization of the catalyst, feed stock used and the operating conditions.

1.1 Transesterification

The triglycerides of the feed oil combine with alcohol in the presence of a catalyst (either acidic or basic) resulting in the formation of another fatty acid ester and glycerol. The final product contains two layers, the top layer being light biodiesel and the bottom heavy layer as glycerol used for cosmetic preparation. The reaction can be represented as

$$RCOOR' + R''OH \xrightarrow{catalyst} RCOOR'' + R'OH$$

Feed oil Alcohol Ester Glycerol

The stoichiometric amount of alcohol to oil is used for the reaction and generally the alcohol to oil molar ratio is 3:1. By using excess alcohol, the reaction will favor the methyl ester formation. Based on the type of feed, acid or base catalyst can be used [15, 22, 24].

2. TYPES OF CATALYSTS USED FOR TRANSESTERIFICATION REACTION

Different types of catalysts are used for the production of biodiesel. The significant features, advantages and disadvantages of the catalysts are explained below.

2.1 Base Catalyst

It has higher catalytic activity, requires shorter time for reaction and mild operating conditions [25]. It has lower cost and easily available [26]. The basic catalyst reacts with the fatty acids present in the oil and forms soap. The soap formed increases the viscosity and ester yield is reduced [27]. The separation and purification steps are difficult to carry out. The process produces a large quantity of wastewater and operating cost increases [25]. Thus, the basic catalyst has these limitations. The commonly used basic catalysts are potassium hydroxide, sodium hydroxide, sodium methoxide and potassium methoxide.

2.2 Acidic Catalyst

These are used when the feed oil contains higher proportion of fatty acids and also water. By using acidic catalysts, both esterification and transesterification can be carried out together [23, 27]. The process requires large ratio of alcohol to oil to carry out the reaction [23]. The biodiesel yield can be improved by changing the operating conditions like alcohol to oil ration, catalyst concentration, reaction time and temperature [28, 29, 30]. The equipment has to resist corrosion because of

acidic conditions [23]. As the reaction to be carried out with larger amount of alcohol, the process needs large size columns. [28]. The acidic catalysts are hydrochloric acid, sulfuric acid and phosphoric acid.

2.3 Homogeneous Catalyst

Homogeneous catalyst exists in the same phase as that of the reaction components and it is soluble with the reactants [31]. It requires shorter time for reaction, can be operated in low severe operating conditions [25]. After the reaction, recovering and regenerating of the catalyst is difficult and expensive process [25]. The process produces large quantity of wastewater [30, 32]. The homogeneous catalyst used for the biodiesel production are sodium methoxide, sodium hydroxide, potassium methoxide, and potassium hydroxide.

2.4 Heterogeneous Catalyst

The catalyst is not utilized during the reaction, and thus can be separated from the reaction mixture. Therefore, the product is free from impurities and it reduces the separation cost [33]. The catalyst can be recovered, reused once again and reduce the overall cost of the process [25, 31]. The biodiesel yield increases and the purity of glycerol improves [20, 29]. It forms three phase mixture of catalyst, alcohol and oil which results in the diffusion limitations [33, 34]. Thus, co-solvent may be used to accelerate the reaction [33]. The commonly used heterogeneous catalyst include zeolite, alumina, MgO, CaO, SrO and BaO [29].

3. PREPARATION AND CHARACTERIZATION OF CATALYST

3.1 Catalyst Preparation

To produce catalyst from biomass derived material, calcination is the commonly known method used. Calcination is thermally treating the material at a higher temperature in the absence of air or oxygen, so that the decomposition of the organic compound takes place into smaller components. The calcination temperature depends on the nature of feedstock and varies in the range of 300 to 1000^{o}C. During the calcination process, calcium carbonate present in the organic compounds undergoes combustion to form CaO and carbon dioxide is released. The smaller particles formed during the above process leads to formation of active sites and thus increases the surface area of the catalyst [25]. The calcination temperature provides the energy required for converting calcium carbonate to calcium oxide. The formation of calcium oxide increases the voids on the surface, and thus pore diameter and pore volume of the catalyst improves [35]. Also, the surface area increases when more of crystal growth of calcium oxide is formed during the calcination. The pore volume increases due to the release of carbonization products along with calcium oxide [36].

Other methods were used for increasing the activity of the prepared catalyst such as co-solvent methods, where the prepared catalyst was treated with a co-solvent which enhances the catalytic activity, and thus the transesterification reaction can be accelerated [37]. Thermal hydration method involves the hydrothermal treatment of the material at an elevated temperature to improve the surface properties [37]. The catalyst surface can be impregnated with support material to enhance the activity. Different factors such as the nature of support material, porosity and internal structure are considered for the impregnation process [32].

3.2 Calcium Oxide as Catalyst

Calcium oxide is prepared by the thermally decomposing minerals like calcite, limestone and from other naturally available sources that has calcium carbonate. The process is carried out by calcination of raw materials containing calcium carbonate

at a higher temperature. During the process, carbon dioxide is released and calcium oxide is formed [38]. Calcium oxide (CaO) is one of the effective catalysts used in the production of biodiesel. A number of waste product streams contain enormous quantity of calcium. It is having low cost, are abundantly available and easily regenerable. It has larger surface area, non-toxic in nature and gives high yield of biodiesel. [4]. The calcium oxide shows the potential of reusability by modifying the used catalyst to different structures [39].

3.3 Characterization of the Catalyst

Thermogravimetric analysis is a technique in which, the mass of the catalyst is measured with respect to time with change in temperature. It gives the description about the various changes happening with the material. It is also employed to study the thermal stability of a material i. e. if a material is thermally stable at a particular temperature, then change in mass of the material is not observed. X-Ray Diffraction (XRD) is method used for analyzing the structure of the crystalline materials, and thus the chemical composition is evaluated. The surface morphology of the catalyst can be investigated using the scanning electron microscopy (SEM) technique [40]. The surface functional groups present on the surface of the catalyst can be studied using Fourier transform infrared spectroscopy (FTIR) [41]. Differential scanning calorimetry (DSC) was used for thermal analysis and for calculating the amount of heat required to raise the temperature of the sample [42]. X-ray fluorescence (XRF) is helpful in determining the elemental composition [43, 44]. BET technique assists in evaluating the surface area, pore volume [41]. The chemical state of various functional groups present and the chemical composition was found using X-ray photoelectron spectroscopy (XPS) [45, 46]. Transmission electron microscopy (TEM) gives the surface image of the catalyst [47].

The various types of catalyst used for the transesterification are studied from the literature. The different types of naturally available materials which can be used for the preparation of the catalyst are investigated. The calcium oxide produced from the natural materials is employed as catalyst. The characterization of the catalyst and the different properties are evaluated using various techniques. The summarization of the naturally available waste materials used for catalyst preparation, calcination conditions, characterization of the catalyst, feedstock used and the operating conditions for the production of biodiesel are shown in table 1.

Table 1: The Summarization of the Materials used for Catalyst Preparation, Preparation Conditions, Characterization Methods, Feedstock used and the Operating Conditions for Biodiesel Production.

Catalyst Precursor	Preparation and Treatment Method	Characterization of the Catalyst	Feed Stock	Operating conditions	% yield	Ref.
Waste egg shell	Calcination temperature 200–1000°C, time 2 h	TGA, XRD and SEMx	Soybean oil	Methanol to oil ratio 9:1, 3 wt% catalyst, 65°C temperature 65°C	95%	[40]
Waste shell of *Turbonillastriatula*	Calcination temperature 600–900°C, time 4 h	TGA, DSC, XRD, SEM-EDX, FTIR	Mustard oil	Methanol to oil ratio 3:1 to 12:1, catalyst 1–3 wt%, temperature 60–70°C	93.3%	[48]

Table 1: Contd.,						
Waste Starfish (Asterinapectinifera)	Calcination at 650°C, 750°C and 850°C for 1 h	XRD, SEM, FTIR	Soybean oil	Methanol to oil ratio 6:1 to 16:1, catalyst to oil ratio 0.03 to 0.1, reaction time 30 to 60 min	91.73%	[49]
Waste capiz shell (*Amusiumcristatum*)	Calcination temperature 900°C, 2 h	XRD, XRF, FTIR analysis	Palm oil	Methanol to oil ratio 1:8, catalyst 1–5%, temperature 60°C	93%	[50]
Rice husk ash	Calcination temperature 900°C, 4 h	XRD, TGA-DTA, SEM, FTIR analysis	Soybean oil	Methanol to oil ratio 3:1 to 24:1, catalyst 1–5 wt%, temperature 30–65°C, time 1–5 h	99.5%	[51]
T striatula waste shells	Calcination at 900°C, doping with barium chloride	XRD, TGA-DSC, BET, SEM, FTIR	Waste cooking oil	Methanol to oil ratio 3:1 to 15:1, catalyst 0.1 to 1.4%, temperature 50–75°C	98%	[52]
Ostrich egg shell	Calcination at 800°C	XRD, BET	Palm oil	Methanol to oil ratio 3:1 to 15:1, catalyst 3 to 10%, reaction time 20 to 180 min, ultrasound irradiation 30 to 80%	92.7%	[53]
Waste fresh water mussel shell	Calcination temperature 900°C, time 3 h	XRD, SEM analysis, BET	Chinese tallow oil	Methanol to oil ratio 7.76:1 to 16.24:1, catalyst concentration 3.59 to 6.41 wt%, temperature 70°C	90%	[54]
Chicken manure	Calcination at 550°C to 950°C	XRD, EDX, FTIR	Waste cooking oil	Methanol to oil 3:1 to 30:1, catalyst loading 2.5 to 20%, mixing speed 800 to 1500	90%	[55]

				rpm, reaction time 60 to 360 min		
Gallus domesticus shell	Calcination at 900°C for 4 h	XRD, BET, SEM, EDX	Waste cooking palm oil	Methanol to oil ratio 5:1 to 25:1, catalyst 1 to 5%, reaction temperature 60 to 100°C, reaction time 60 to 300 min	90.1%	[57]
T. jourdani shells	Calcination at 900°C for 5 h	XRD, TGA, FTIR, SEM	Palm oil	Methanol to oil ratio 1:1 to 9:1, catalyst 3 to 15%, time 3 to 7 h	99.33%	[58]
Egg shell	Calcination at 800°C for 24 h	XRD, SEM, XRF	Waste vegetable oil	Methanol to oil 9.89:1 to 35.11:1, catalyst 0.98 to 6.02%, temperature 56.6 to 73.4°C, time 330 min	91%	[43]
Waste crab shell	Calcination at 900°C and impregnated on Na-ZSM-5	XRD, BET	Neem oil	Methanol to oil 3:1 to 15:1, catalyst 5 to 15%, reaction time 2 to 8 h	95%	[59]
Pomacea sp. shell	Calcination at 900°C for 2 h	XRF, FTIR, XRD	Palm oil	Methanol to oil ratio 5:1 to 11:1, catalyst 1 to 5%, reaction time 1 to 4h	95.61%	[44]
TamarindusIndica fruit shell	Calcination at 800°C for 3 h	XRF, SEM, EDX, BET	*Parinaricuratellifolia* seeds oil	Methanol to oil 3:1 to 12:1, catalyst 1 to 6%, reaction time 1 to 4 h, temperature 60°C	96.2%	[60]
Coconut coir husk	The material was sulfonated with sulphuric acid at 100°C for 1h	EDX, SEM, FTIR, XPS, TGA	Waste palm oil	Methanol to oil ratio 12:1, catalyst 5 to 20%, reaction temperature 90°C to 150°C, reaction time 1 to 4h	89.8%	[45]
Egg shell	Calcination at	XRD, FTIR, SEM,	Waste frying oil	Methanol to	95.05%	[61]

	900°C for 2.5 h	EDX, BET		oil ratio 3:1 to 12:1, catalyst 1 to 4%, temperature 50°C to 70°C, time 30 to 180 min		
waste mud crab (*Scylla serrata*) shell	Dried at 105°C	XRD, SEM-EDX, BET	palm olein	Methanol to oil ratio 0.25 to 0.75, catalyst 1.6-8.4 wt%, temperature 40–90°C, stirring speed 330-670 rpm	98.8%	[40]
Waste chicken egg shells	Calcination at 900°C for 1 h	SEM, BET	Catfish oil (*Pangasius hypothalamus*)	Methanol to oil ratio 6:1 to 15:1, catalyst 1 to 3%	87.77%	
			Waste cooking oil		96.23%	[62]
Ceibapentandra Stalk	Sulfonation followed by carbonization at 523 K for 2h	SEM, EDX, FTIR, XRD, TGA	*Sterculiafoetida* Seed Oil	Methanol to oil ratio 6:1 to 18:1, catalyst 0.5 to 5.5%, reaction time 0.5 to 3 h, temperature 468–498 K	97%	[59]
Red banana peduncle	Calcination at 700°C for 4 h	SEM, EDX, BET, XRD, FTIR	Ceibapentandra oil	Methanol to oil ratio 3.27:1 to 16.73:1, catalyst 0.82 to 4.18%, reaction time 12.73 to 147.27 min	97.54%	[18]
Coconut shell	Carbonization followed by sulfonation of the material with sulphuric acid	BET, SEM	Palm oil	Methanol to oil 30:1, catalyst 6%, time 6 h	88.15%	[64]
Waste egg shell	Calcination at 900°C for 4 h	XRD, BET, SEM, FTIR	Eucalyptus oil	Methanol to oil ratio 6:1 to 15:1, catalyst 1 to 12%, reaction time 1.5 h, temperature 55°C	70.5%	
	Calcined sample				93.2%	[16]

	impregnated on mixed metal oxides					
Waste date pits	Calcination at 450°C for 4h	XRD, SEM, EDX, XPS, BET	Date pits oil	Methanol to oil ratio 6:1 to 18:1, catalyst 1.5 to 7.5%, temperature 55°C to 75°C	98.2%	[46]
Calcined waste chicken and fish bones	Calcination at 1000°C for 4h	SEM, BET, FTIR, TGA, XRD	Used cooking oil	Methanol to oil ratio 10:1, catalyst 0.66 to 2.34%, temperature 40°C to 90°C, time 0.66 to 2.34 h	89.5%	[61]
Egg shells	Calcination at 900°C for 4h and treated with 1-5wt% of Fe_3O_4 nanoparticles	TGA, XRD, SEM, TEM, FTIR, BET, VSM	*Pongamiapinnatta* oil	Methanol to oil ratio 3:1 to 15:1, catalyst 0.5 to 2.5%, temperature 45°C to 70°C, time 0.5 to 2.5 h	98%	[47]
Donaxdeltoides shells	Calcination at 900°C for 3h	SEM, EDAX, XRD, FTIR	*Calophyllum inophyllum*-waste cooking oil	Methanol to oil ratio 55.18:1 to 88.82:1, catalyst 4.64 to 11.36%, time 99.6 to 200.5 min	96.5%	[66]
Chicken egg shells	Calcination at 850°C for 3h and subjected to sonication	SEM, BET, XRD, FTIR	Waste cooking oil	Methanol to oil 8:1 to 14:1, catalyst 1 to 4%, temperature 50°C to 70°C, agitation speed 200 to 500 rpm	93.10	[67]
Chicken eggshells	Calcination at 500 to 110°C for 3h	XRF, TGA, FTIR, SEM, BET	Soybean oil	Methanol to oil ratio 6:1 to 14:1, catalyst 2 to 12%, temperature 45°C to 70°C, time 1 to 5h	93%	[68]
Turbo jourdani shells	Calcination at 900°C for 3h	XRD, FTIR, TGA, SEM	Palm oil	Methanol to oil 1:1 to 9:1, catalyst 3 to 15%, time 3 to 7h	99.33%	[58]
Waste egg shells	Calcination at 400°C to	TGA, XRD, EDX, TEM, FTIR, BET	Sunflower waste cooking oil	Methanol to oil ratio 6:1	97.5%	[69]

	1100°C for 2h			to 12:1, catalyst 3 to 9%, time 30 to 120 min, speed 200 to 400 rpm		

4. CONCLUSIONS

The current study reviews the production of biodiesel from various feedstocks and addressed the issue of depleting non-renewable resources. The cost of catalyst is one of the major concern in the transesterification process. The above problem is resolved by producing catalyst from naturally available waste materials. This reduce the cost of the process and the properties have also improved. The calcium oxide obtained from the calcination process can be efficiently used as catalyst for biodiesel production. It has lower cost, can be easily regenerated and can be altered to various structures. The catalyst will also enhance the yield of biodiesel. Therefore, the catalyst obtained naturally available waste materials, is successful in reducing the cost of the process and also to enhance the production of biodiesel.

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